Synthesis of Semiconductor and Metal Oxide Nanoparticles by Laser Vaporization-Controlled Condensation Techniques

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Nanoparticles often exhibit novel properties, which are different from the bulk materials' properties.^[1] Many of these properties show strong dependence on size, shape and surface preparation. [1] The characterization of these properties can ultimately lead to identifying many potential uses, particularly in the field of catalysis. Research in this area is motivated by the possibility of designing nanostructured materials that possess novel electronic, optical, magnetic, photochemical and catalytic properties. Such materials are essential for technological advances in photonics, quantum electronics, nonlinear optics and information storage and processing. We have developed a novel technique to synthesize nanoparticles of controlled size and composition. [2-4] Our technique combines the advantages of pulsed laser vaporization with controlled condensation (LVCC) in a diffusion cloud chamber under well-defined conditions of temperature and pressure. It allows the synthesis of a wide variety of nanoparticles of metal oxides, carbides and nitrides. Furthermore, the same method can be coupled to plasma and ionic polymerization techniques, thus allowing the incorporation of the metallic nanoparticles within the polymer films. We will present some new results on the photoluminescence (PL) properties of the Si nanocrystals. One of the main goals of this work is to compare the results of the PL from the solid surface-oxidized particles, which we previously studied, with those from the incorporated particles in polymer films. We also present evidence for the photoreduction of the white WO₃ nanoparticles into the blue W₂O₅ upon irradiation with the second harmonic of the Nd:YAG laser.

Web-like aggregates of coalesced Si nanocrystals have been produced by the LVCC technique. SEM micrographs show particles with ~ 5-8 nm diameters but the Raman shift suggests the presence of particles as small as ~ 4 nm. The particles show luminescence properties that are similar to those of porous Si and Si nanoparticles produced by other techniques. They show a short-lived blue emission characteristic of the ${\rm SiO}_x$ coating and a longer-lived red emission. The short lifetime component of the red emission, about 12 μs , does not depend on emission wavelength. The longer-lived component has a lifetime that ranges from 90 to over 130 μs (at 300 °K), increasing with emission wavelength. Different methods to incorporate the Si nanocrystals into polymeric films of polystyrene and polyvinyl acetate have been used. The quenching of the photoluminescence of the nanoparticles by different organic electron acceptors in solution has also been investigated. The quenching effect results in decreasing both the intensity and the lifetime of the red emission. The results suggest an electron transfer mechanism for the photoluminescence quenching.

Tungsten oxide is known as a photochromic and electrochromic material since it changes color upon the absorption of light and in response to an electrically induced change in oxidation state. We found that the white tungsten oxide nanoparticles prepared by the LVCC method change color to blue by irradiation with the second harmonic of the Nd:YAG laser (532 nm) in air. The IR and Raman spectra measured after irradiation show clearly all the features associated with the reduction of WO_3 into W_2O_5 nanoparticles. These features include the decrease in the absorption band at 800 cm⁻¹ and the disappearance of the Raman bands at 802 cm⁻¹ and 716 cm⁻¹, which are the characteristic IR and Raman features of WO_3 . The observed laser induced reaction of the white

 WO_3 nanoparticles appears to be a multiphoton process. We observed an interesting quenching effect by the WO_3 nanoparticles. The PL spectra taken from colloid solutions of the Si nanocrystals in ethanol after successive additions of WO_3 particles and excitations with 266 nm show systematic loss of the PL intensity with increasing the concentration of the WO_3 nanoparticles. This quenching effect can be explained by an electron transfer mechanism from the Si to the WO_3 nanoparticles.

References

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